

PATENT SPECIFICATION

NO DRAWINGS

Inventors: ARTHUR WESLEY RAVENSCROFT and ALFRED JOHN RUDGE



825.185

Date of filing Complete Specification: May 21, 1958.

Application Date: May 31, 1957.

No. 17313/57.

Complete Specification Published: Dec. 9, 1959.

Index at acceptance:—Classes 1(2), B1D; and 90, K3F.

International Classification:—C01b.

COMPLETE SPECIFICATION

Improvements in or relating to the Purification of Electrolytic Fluorine

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved step in a process for the electrolytic manufacture of fluorine wherein the hydrogen fluoride impurity in the fluorine is removed.

Fluorine produced by the electrolysis of molten mixtures of potassium fluoride and hydrogen fluoride is contaminated with hydrogen fluoride. The concentration of hydrogen fluoride contaminant in the fluorine depends on various factors, particularly, the concentration of hydrogen fluoride in the electrolyte and the electrolyte temperature. Various methods have been adopted for removing this undesired hydrogen fluoride contaminant. One such method involves cooling the contaminated fluorine to condense the hydrogen fluoride. However to condense a major proportion of the hydrogen fluoride contaminant calls for very low temperature conditions and this is an expensive procedure.

Again it is known that sodium fluoride which is available commercially, for example, in powder form can absorb hydrogen fluoride and it is also known that sodium hydrogen fluoride NaF.HF which can be formed by absorption of the hydrogen fluoride by sodium fluoride can be decomposed by heating to give sodium fluoride and hydrogen fluoride. It would thus appear that this might suggest the basis for a method for the removal of the hydrogen fluoride contaminant in fluorine. To adopt such a method could involve passing the contaminated fluorine over sodium fluoride powder in a first scrubbing zone to remove the bulk of the HF. The fluorine could then

be passed through a second scrubbing zone comprising a tower packed with sodium fluoride pellets to provide more intimate contact with the incoming gas and to remove any residual hydrogen fluoride. However, with absorption of HF the aforementioned powder swells and cakes and this would normally be removed from the first scrubbing zone at short intervals and be replaced by fresh powder. Such a procedure, especially the recharging procedure is a cumbersome, unpleasant as well as an expensive operation.

One apparently simple alternative, namely to utilise sodium fluoride pellets to remove the whole of the hydrogen fluoride, is not, in this simple form, practicable, because on absorbing the hydrogen fluoride the pellets swell and could block the absorption tower.

U.S. Specification No. 2,426,558 describes a method of circumventing this difficulty. This involves first screening commercial crystalline sodium bifluoride (NaF.HF) to remove coarse particles or aggregates, and pelleting the screened material at a pressure to give a material of a particular apparent density. The pellets are then heated until most of the HF is removed, preferably until porous sodium fluoride pellets again of a particular apparent density are obtained. The gas containing HF is passed through a series of absorption chambers containing the porous pellets heated to a temperature of at least 85°C . and preferably not lower than 100°C . so that by this means the porous sodium fluoride pellets do not swell and disintegrate and absorption beyond the stage where NaF.HF is formed is prevented. Thereafter the gas may be passed through one or more chambers containing the pellets maintained at temperatures below 85°C . to remove residual HF. The spent pellets may then be heated to regenerate the porous sodium fluoride pellets. This method involves considerable expense in

[Pri.

preforming these particular porous sodium fluoride pellets and in maintaining the pellets at elevated temperature. Again the capacity of sodium fluoride for absorbing hydrogen fluoride decreases with increase of temperature and since the first series of chambers is maintained at a temperature of at least 85° C. the sodium fluoride is in fact being employed at a temperature at which its absorptive capacity for hydrogen fluoride is reduced. Moreover when using this process for removal of HF in fluorine it is our experience that the hydrogen fluoride content was not reduced to below 3% to 4% by volume of the fluorine.

We have now found surprisingly that sodium fluoride powder after absorption of hydrogen fluoride contaminant in fluorine may be continually regenerated with substantially no loss in absorptive properties and this regenerating procedure may be very conveniently carried out *in situ*.

According to the present invention therefore we claim in a process for the electrolytic manufacture of fluorine the improved steps of removing hydrogen fluoride contaminant in fluorine by bringing the contaminated fluorine into contact with sodium fluoride powder at a temperature which is at least 0° C. but less than 85° C. and after absorption of hydrogen fluoride regenerating the absorbent by heating the same, and continually repeating the steps of removing hydrogen fluoride contaminant in fluorine by means of the regenerated absorbent at said temperatures and regenerating the absorbent by heating.

Although the temperature for absorption of the hydrogen fluoride may vary within the disclosed range it is preferred to carry out the absorption procedure at temperatures within the narrower range 0° C. to 40° C. and it is particularly preferred to carry out the absorption at normal atmospheric temperature.

Preferably the absorbent is regenerated *in situ*.

Suitably the absorbent is regenerated by heating at a temperature in the range 200° C. to 400° C. and preferably in the range 300° C. to 400° C.

Various means may be adopted using different types of apparatus to carry out the process of the invention. Thus in one method of carrying out the invention there is provided a scrubbing zone wherein the contaminated fluorine is passed at normal temperature over a series of several superimposed horizontal shelves containing trays having shallow beds of sodium fluoride powder. Suitable means are provided for regenerating the spent absorbent *in situ* by heating said absorbent up to a temperature of approximately 400° C. For example, one such means may comprise an electrical heating cable in the shape of a grid situated beneath each layer of trays or the cable may be situated in the interior of a shallow bed of the absorbent.

Other than electrical heating means may also be employed to effect regeneration of the absorbent. During the regeneration procedure it is desirable to pass a small amount of an inert gas such as nitrogen or air over the absorbent to remove the hydrogen fluoride as it is evolved. The hydrogen fluoride may then be optionally recovered from the gas in which it is entrained. In general practice two units are employed, one serving to absorb the hydrogen fluoride while the other is being regenerated.

When the fluorine purified by the present process still contains small amounts of hydrogen fluoride the latter may be removed by known means. For instance the slightly contaminated fluorine may be passed through a vertical tower packed with pellets made from sodium fluoride powder, suitably maintained at normal temperature. This sodium fluoride can conveniently be ordinary commercial grade. Due to the small amount of HF left in the fluorine purified according to the invention any blocking due to absorption and swelling of sodium fluoride in such a tower would only take place after very lengthy periods of time.

The following Examples illustrate the invention.

EXAMPLE 1.

Fluorine containing HF contaminant evolved from an electrolytic cell was passed through a vessel containing two trays having a layer of sodium fluoride $\frac{1}{4}$ inch deep. From time to time the trays were removed and weighed and the increase in weight due to absorption of HF noted. They were then replaced in the scrubber and the scrubber heated in a gas furnace at 300° C. to 350° C. for $\frac{1}{2}$ hour. Nitrogen was passed at about a quarter of the fluorine rate through the vessel during this heating period in the reverse direction to that in which the contaminated fluorine was passed. The trays were then reweighed, replaced in the scrubber and the cycle of removing HF and regenerating the absorbent was twice repeated. In the fourth cycle hydrogen fluoride itself was passed through the system to determine whether this would have any deleterious effect on the subsequent efficiency of the absorbent. As shown in the table below no such effect was observed. The fluorine rates and the HF content (% v/v) of the fluorine in the 5 cycles were as follows: (1) 2.5 l/hr. and 24%, (2) 6.3 l/hr. and 7%, (3) 12.5 l/hr. and 9%, (4) here only HF was passed through the system, (5) 12.5 l/hr. and 20%. The initial weight of NaF in the first and second trays was 73 g. and 70 g. respectively.

In this Example and the following Examples the flow rates are calculated from the fluorine cell amperage assuming a 100% current efficiency. The percentage of HF in the fluorine is calculated from the fluorine flow rate and the weight of HF absorbed in the

trays. As in some cycles a small percentage of hydrogen fluoride passed through the scrubbers, this figure is an approximate one. In each run the physical form of the sodium fluoride changed considerably. The first absorption resulted in sodium fluoride swelling and rising from the bottom of the tray. On heating, the surface of the absorbent caked and cracked slightly. Succeeding absorptions resulted in very little swelling but on heating further cracking occurred until after three or

four cycles, the whole mass had broken up into flakes. The results of the run are shown in the table. In the table in this and the following Examples where under the heading of "Tray 1," "Tray 2" and "Tray 3" % is mentioned, this means either the percentage by weight of HF absorbed by the sodium fluoride or the percentage by weight of HF remaining in the sodium fluoride absorbent after heating.

Cycle No.	Tray 1				Tray 2		% of total HF absorbed in Tray 1
	HF absorbed by NaF		HF in NaF after heating		HF absorbed by NaF		
	(g)	(%)	(g)	(%)	(g)	(%)	
1	41.1	36.0	2.6	3.4	5.7	7.5	88
2	5.5	7.0	0.0	0.0	0.0	0.0	100
3	24.9	25.4	0.6	0.8	0.3	0.4	99
4	67.5	40.0	0.3	0.4	18.1	20.5	79
5	43.3	37.2	0.0	0.0	9.7	12.2	82

It will be observed that the sodium fluoride after repeated regeneration maintained an excellent absorptive capacity for hydrogen fluoride.

EXAMPLE 2.

Fluorine containing HF contaminant from an electrolytic cell was passed through a vessel containing a tray 2 inches deep having a bed of sodium fluoride powder 1 inch deep. The fluorine was then passed through a second vessel containing two trays each having a $\frac{1}{4}$ inch bed of powder. The sodium fluoride in trays 2 and 3 contained in the second vessel was replaced after each cycle. From time to time the tray in the first vessel was removed and weighed and the increase due to absorption of HF noted. The tray was then replaced

in the first vessel which was heated for 2 hours at 350° C. to 400° C., nitrogen being passed through the scrubber during the heating period in the reverse direction to that of the contaminated fluorine and at about a quarter of the flow rate. The trays were then reweighed, replaced in the scrubber and the cycles repeated. The fluorine rate and the HF content (% v/v) of the fluorine in the six cycles were as follows: (1) 13 l/hr. and 43%, (2) 12 l/hr. and 21%, (3) 13 l/hr. and 20%, (4) 14 l/hr. and %, (5) 13 l/hr. and 22%, (6) 17 l/hr. and 25%. The initial weights of NaF in the trays 1, 2 and 3 were 524 g., 135 g., and 97 g. respectively. The results of the run are shown in the table.

Cycle No.	Tray 1				Tray 2		Tray 3		% of total HF absorbed in Tray 1
	HF absorbed by NaF		HF in HaF after heating		HF absorbed by NaF		HF absorbed by NaF		
	(g)	(%)	(g)	(%)	(g)	(%)	(g)	(%)	
1	157	22.5	0.0	0.0	2.7	2.0	1.0	1.0	98
2	51	8.6	1.0	0.2	3.3	2.4	0.0	0.0	94
3	72.5	11.8	0.0	0.0	7.5	5.3	1.5	1.5	89
4	62	10.3	0.0	0.0	5.0	3.5	0.5	0.5	92
5	102	15.8	0.0	0.0	7.3	5.1	0.6	0.6	93
6	76	12.3			4.5	3.2	1.4	1.4	93

It will be apparent that there had been very efficient removal of the bulk of the HF contaminant in the fluorine after passing through tray 1 and that more of the residual amounts of HF in the fluorine was removed by passing through trays 2 and 3. It is also apparent that the sodium fluoride in tray 1 after repeated regeneration maintained an excellent absorptive capacity for hydrogen fluoride.

EXAMPLE 3.

Fluorine containing HF contaminant from an electrolytic cell was passed through a vessel containing a tray 2 inches deep having a bed of sodium fluoride powder 1 inch deep. The fluorine was then passed through another vessel containing a second tray having a bed of sodium fluoride powder $\frac{1}{4}$ inch deep. The sodium fluoride in the second tray was replaced after each cycle. From time to time the tray in the first vessel was removed and weighed and the increase due to absorption of

HF noted. The tray was then replaced and the scrubber heated at various temperatures and for various periods of time, nitrogen being passed through the scrubber during the heating period in the reverse direction to that of the contaminated fluorine and at about a quarter of the fluorine flow rate. The tray was then reweighed, replaced in the scrubber and the cycle repeated several times. The fluorine rate and the HF content (% v/v) of the fluorine in the six cycles were as follows: (1) 26 l/hr. and 12%, (2) 8.7 l/hr. and 19%, (3) 26 l/hr. and 16%, (4) 26 l/hr. and 13%, (5) 26 l/hr. and 13%, (6) 26 l/hr. and 24%. The initial weight of sodium fluoride powder in trays 1 and 2 were 357 g. and 120 g. respectively. The results obtained are shown in the table below. In cycles 1 to 4 the absorbent was regenerated by heating at 350° C. for 2 hours; in cycle 5 it was heated at 600° C. for 2½ hours and in cycle 6 was heated at 450° C. to 680° C. for 2 hours.

Cycle No.	Tray 1				Tray 2		% of total HF absorbed in Tray 1
	HF absorbed by NaF		HF in NaF after heating		HF absorbed by NaF		
	(g)	(%)	(g)	(%)	(g)	(%)	
1	52.8	12.9	8.9	2.4	7.8	6.1	87
2	33.3	8.5	-0.5	0.0	3.1	2.5	92
3	72.8	16.9	2.2	0.6	14.1	10.5	84
4	64.4	15.3	18.3	4.8	4.8	3.8	93
5	64.3	15.2	0.0	0.0	4.8	3.8	93
6	118.4	24.9	6.3	1.7	7.2	5.7	94

It will be observed that the sodium fluoride in tray 1 after repeated regeneration maintained an excellent absorptive capacity for hydrogen fluoride.

5 Following cycle 5 in which the absorbent was heated to a high temperature of 600° C. it was found that this had no effect on the absorptive powers of the sodium fluoride in the subsequent cycle. Further cycles showed, 10 however, that the use of this high temperature ultimately reduced the absorptive efficiency of the sodium fluoride. It will be apparent that there had been a very efficient removal of HF from the fluorine after passing through tray 1 15 and that more of the small amount of residual HF in the fluorine was removed on passing through tray 2.

WHAT WE CLAIM IS:—

1. In a process for the electrolytic manu- 20 facture of fluorine the steps of removing hydrogen fluoride contaminant in fluorine which comprise bringing the contaminated fluorine into contact with sodium fluoride powder at a temperature which is at least 0° 25 C. but less than 85° C. and after absorption of hydrogen fluoride regenerating the absorbent by heating the same and continually repeating the steps of removing hydrogen fluoride con- 30 taminant in fluorine by means of the re-generated absorbent at said temperatures and regenerating the absorbent by heating.

2. The process according to claim 1 in

which the absorption temperature is within the range 0° C. to 40° C. and which is preferably 35 normal atmospheric temperature.

3. The process according to claim 1 or claim 2 in which the absorbent is regenerated by heating *in situ*.

4. The process according to any of the preceding claims in which the absorbent is re- 40 generated by heating at a temperature in the range 200° C. to 400° C. and preferably in the range 300° C. to 400° C.

5. The process according to any of the preceding claims in which the contaminated 45 fluorine is passed over a series of several superimposed horizontal shelves containing trays containing shallow beds of sodium fluoride powder and in which the heating means for regenerating the absorbent com- 50 prises electrical heating cable in the shape of a grid situated beneath each layer of trays or an electrical heating cable situated in the interior of the bed of the sodium fluoride 55 absorbent.

6. In a process for the electrolytic manu- facture of fluorine the steps of removing hydrogen fluoride contaminant in fluorine as 60 described in Examples 1, 2 and 3.

7. Fluorine whenever purified from 60 hydrogen fluoride contaminant as described in any of the preceding claims.

ALFRED O. BALL,
Agent for the Applicants.

PROVISIONAL SPECIFICATION

Improvements in or relating to the Purification of Electrolytic Fluorine

We, IMPERIAL CHEMICAL INDUSTRIES 65 LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare this invention to be described in the following statement:—

This invention relates to an improved step 70 in a process for the electrolytic manufacture of fluorine wherein the hydrogen fluoride impurity in the fluorine is removed.

Fluorine produced by the electrolysis of molten mixtures of potassium fluoride and hydrogen fluoride is contaminated with 75 hydrogen fluoride. The concentration of hydrogen fluoride contaminant in the fluorine depends on various factors, particularly, the concentration of hydrogen fluoride in the electrolyte and the electrolyte temperature. 80 Various methods have been adopted for removing this undesired hydrogen fluoride contaminant. One such method involves cooling the contaminated fluorine to condense the hydrogen fluoride. However to condense a 85 major proportion of the hydrogen fluoride contaminant calls for very low temperature conditions and this is an expensive procedure.

Again it is known that sodium fluoride which is available commercially, for example,

90 in powdered form can absorb hydrogen fluoride and it is also known that sodium hydrogen fluoride NaF.HF which can be formed by absorption of the hydrogen fluoride by sodium fluoride can be decomposed by 95 heating to give sodium fluoride and hydrogen fluoride. It would thus appear that this might suggest the basis for a method for the removal of the hydrogen fluoride contaminant in fluorine. To adopt such a method could involve 100 passing the contaminated fluorine over sodium fluoride powder to remove the bulk of the HF. The fluorine could then be passed through a tower packed with sodium fluoride pellets to provide more intimate contact with the in- 105 coming gas and to remove any residual hydrogen fluoride. However, with absorption of HF the aforementioned powder swells and cakes and this would normally be removed 110 from the first scrubbing zone at short intervals and be replaced by fresh powder. Such a procedure, especially the recharging procedure is a cumbersome, unpleasant as well as an ex- 115 pensive operation.

One apparently simple alternative, namely to utilise sodium fluoride pellets to remove the whole of the hydrogen fluoride, is not, in this

simple form, practicable, because on absorbing the hydrogen fluoride the pellets swell and could block the absorption tower.

5 U.S. Specification No. 2,426,558 describes a method of circumventing this difficulty. This involves first screening commercial crystalline sodium bifluoride (NaF.HF) to remove coarse particles or aggregates, and pelleting the screened material at a pressure to give a
10 material of a particular apparent density. The pellets are then heated until most of the HF is removed, preferably until porous sodium fluoride pellets again of a particular apparent density are obtained. The gas containing HF
15 is passed through a series of absorption chambers containing the porous pellets heated to a temperature of at least 85°C . and preferably not lower than 100°C . so that by
20 this means the porous sodium fluoride pellets do not swell and disintegrate and absorption beyond the stage where NaF.HF is formed is prevented. Thereafter the gas may be passed through one or more chambers containing the
25 pellets maintained at temperatures below 85°C . to remove residual HF. The spent pellets may then be heated to regenerate the porous sodium fluoride pellets. This method involves considerable expense in preforming these
30 particular porous sodium fluoride pellets and in maintaining the pellets at elevated temperature. Again the capacity of sodium fluoride for absorbing hydrogen fluoride decreases with increase of temperature and since the first
35 series of chambers is maintained at a temperature of at least 85°C . the sodium fluoride is in fact being employed at a temperature at which its absorptive capacity for hydrogen fluoride is reduced. Moreover when using this
40 process for removal of HF in fluorine it is our experience that the hydrogen fluoride content was not reduced to below 3% to 4% by volume of the fluorine.

As an improved step in a process for the

electrolytic production of fluorine we have now found surprisingly that the hydrogen fluoride contaminant in the evolved fluorine
45 may be removed in a convenient manner by contacting the contaminated fluorine with sodium fluoride powder and that after the sodium fluoride powder has caked after
50 absorbing an appropriate amount of hydrogen fluoride, the caked material may be repeatedly regenerated by heating, conveniently, *in situ*, and further employed for the absorption of
55 the hydrogen fluoride contaminant in the fluorine.

In one method of carrying out the invention there is provided a scrubbing zone wherein the contaminated fluorine passes over a series
60 of several superimposed horizontal shelves containing shallow trays of sodium fluoride powder. The powder is not maintained at elevated temperature while passing the contaminated fluorine through the scrubber. Some
65 suitable means is, however, provided for regenerating the spent absorbent *in situ* by heating the same up to a temperature of about 400°C . For example, one such means may comprise a nickel or monel sheathed heating
70 cable in the shape of a grid beneath each layer of trays, although other procedures relying, for example, on other than electrical heating means can be employed to effect regeneration of the spent absorbent. A second absorption
75 zone is also provided so that while one zone is in use, regeneration of spent, caked, sodium fluoride absorbent can take place in the other. After passing through the first absorption zone
80 the fluorine can then be passed through a vertical tower packed with pellets made from the ordinary commercial grade sodium fluoride powder to remove any residual hydrogen fluoride from the fluorine.

ALFRED O. BALL,
Agent for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1959.
Published by The Patent Office, 25, Southampton Buildings, London, W.C.2, from which
copies may be obtained.